

## Theoretical Formalism That Describes (I-t) Curves

### Where the Presence of Diffusion Limited 3D Nucleation and HER Appear Simultaneously

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During the electrodeposition of metals (M) from aqueous solutions containing their ions ( $M_{(ac)}^{z+}$ ), is a common occurrence that secondary reactions, which are generally undesirable, take place simultaneously, such as the well known Hydrogen Evolution Reaction (HER).

This kind of reaction gives rise to a cathodic efficiency for the deposition process, which is much lower than 100%. For example during chromium deposition this is approximately equal to 30% [1]. For very many cases of metal deposition [2] the influence of HER is a hindrance to study the process by means of the analysis of the potentiostatic current transients, as under the circumstances their experimental nature is too complex and cannot be described by any of the existing theories [3]. The main reason for the lack in agreement between the latter and the description for the experimental transients, is that the theories aimed at describing the electrocrystallization of metals, considering solely the faradaic process for the reduction of the ( $M_{(ac)}^{z+}$ ) ions.

Therefore it would be of great interest to have a theoretical formalism capable of describing the electrocrystallization process for metals when there occurs simultaneously another redox reaction, particularly HER. Regarding this, there has been attempts [4] which aimed at describing the influence of redox processes upon the current potentiostatic transients due to a nucleation process (2D or 3D) for metals, limited by the incorporation of adatoms to growth centres; however the large amount of experimental evidence existing, has shown very numerous cases in which the electrodeposition of metals takes place via multiple nucleation with diffusion limited 3D growth [5-7]. Hence, it is the aim of the present work to present a theoretical formalism capable of describing the process for electrocrystallization of metals when it occurs by means of multiple diffusion limited nucleation, where other reduction reactions take place over the surface of the nuclei (protons in particular).

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